Journal of Industrial and Engineering Chemistry xxx (2017) xxx-xxx



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry



journal homepage: www.elsevier.com/locate/jiec

Application of the commercial ion exchange membranes in the all-vanadium redox flow battery

Gab-Jin Hwang^{a,*}, Sang-Won Kim^b, Dae-Min In^a, Dae-Yeop Lee^a, Cheol-Hwi Ryu^a

^a Grad. School, Dept. Green Energy Eng., Hoseo University, Asan, Chungnam, 314-99, Republic of Korea

^b Green Tech. Team, Korea Institute of Science and Technology Europe, Campus E72, Universitat des Saarlandes, 66123, Germany

ARTICLE INFO

Article history: Received 19 June 2017 Received in revised form 9 November 2017 Accepted 18 November 2017 Available online xxx

Keywords: Energy storage Redox flow battery Vanadium Ion exchange membrane Cell performance

Introduction

A power system using renewable energy such as a solar and wind needs an energy storage system because of its low energy density and intermittent nature. A redox flow battery (RFB) is being investigated as an energy storage system for a load leveling and an emergency uninterruptable power supplies [1-4]. A RFB is able to store electrical energy in the form of chemical energy and convert that into electricity [4–6]. One advantage of a RFB is that the power and energy storage capacity can be increase easily. Recently, the all-vanadium redox flow battery (VRFB) is being investigated for an

energy storage system [1–6]. In a VRFB energy storage system, an ion exchange membrane (IEM) is the key component. A high membrane resistance causes a large internal iR drop, and the iR losses through the membrane lead to low voltage efficiency of the VRFB. Therefore, the high permeability of the vanadium ions $(V^{2+}, V^{3+}, VO^{2+}, VO_2^+)$ through a membrane lead to low current efficiency due to the selfdischarge of the permeated vanadium ion through a membrane [2,3]. An IEM should possess a low membrane resistance to minimize losses in voltage efficiency, and should exhibit low permeation rates of the active species to minimize self-discharge. Finally, the IEM should also have a good chemical stability and be low in cost [2,3,7,8]. Nafion series (produced by DuPont) which was

Corresponding author. E-mail address: gjhwang@hoseo.edu (G.-J. Hwang).

ABSTRACT

Three commercial anion exchange membranes and two commercial cation exchange membranes were tested to use as a separator in the all-vanadium redox flow battery (VRFB). Membrane properties such as an ionic conductivity and a permeability of each vanadium ion were evaluated. Ionic conductivities decreased in the order: Nafion117 \approx APS > NEPEM115 > FAP-PP-475 > FAP-PE-420. An anion exchange membrane had a low permeability of each vanadium ion compared to a cation exchange membrane. Energy efficiencies of VRFB using the commercial ion exchanges membrane had almost the same value in the range of 76.0-78.7%.

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> based on fluorine, shows an excellent chemical stability in VRFB, but the voltage efficiency of VRFB using Nafion (cation exchange membrane) decreases with the increasing membrane resistance for a long cycle [7]. Furthermore, the cost of Nafion is very high. Many researchers are being investigated an IEM based on hydrocarbon to achieve a good chemical stability, a low permeability of vanadium ions, and a low cost [9-20]. However, those membranes exhibiting good electrochemical cell performance need the more time for the commercialization in the market. Therefore, the selection of the suitable membrane in a commercial ion exchange membrane as a separator need to commercialize a VRFB with the stacking and scale-up.

> In this research, the membrane properties such as a membrane resistance and permeability of the vanadium ions in the commercial ion exchange membranes based on hydrocarbon were tested. And, performances of VRFB using the commercial ion exchange membranes were evaluated.

Experimental

Membrane properties of commercial ion exchange membranes

Membrane resistance

The commercial ion exchange membranes (FAP series from Fumatech Co., NEPEM115 from Kerun Co., APS from Asahi Glass Co. and Nafion117 from Dupont) were measured its membrane resistance. A membrane resistance was measured in $1 \text{ M} (\text{mol } L^{-1})$ H₂SO₄ aqueous solution.

https://doi.org/10.1016/i.jiec.2017.11.023

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Please cite this article in press as: G.-J. Hwang, et al., Application of the commercial ion exchange membranes in the all-vanadium redox flow battery, J. Ind. Eng. Chem. (2017), https://doi.org/10.1016/j.jiec.2017.11.023

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Nomenc	Nomenclature	
A	Membrane area, cm ²	
C _A	Molarity of the vanadium ion in the vanadium ion solution, mol	
C _B	Molarity of the vanadium ion in the H ₂ SO ₄ solution after the certain time, mol	
e _{ac} , e _{ad}	Average cell voltage for charge and discharge, respectively, V	
IC	Ionic conductivity, S cm ⁻¹	
Ĺ	Membrane thickness, mm	
2 C	Permeability, cm ² min ⁻¹	
Q _C , Q _D	Quantity of the coulomb for charge and discharge, respectively, C	
R	Membrane resistance in 1 M H_2SO_4 aqueous solution, Ωcm^2	
R ₁ , R ₂	Electric resistance of the conductivity cell with membrane and without membrane, respectively, Ω	
S	Effective membrane area, cm ²	
t	Time, min	
V _B	Volume of H_2SO_4 solution, cm ³	
lc	Current efficiency, %	
lv	Voltage efficiency, %	
$\eta_{\rm E}$	Energy efficiency, %	

The measurement method and experimental apparatus for a membrane resistance in 1 M H₂SO₄ aqueous solution are the same with the previous paper [2,3,7]. A membrane resistance of the conductivity cell as shown in Fig. 1 with a membrane (R₁) and without a membrane (R₂) was measured at room temperature using an LCR meter (PM-6304, Furuka Co.). Each compartment of the cell was filled with 1 M H₂SO₄ aqueous solution and both solutions were circulated. The effective membrane area (S) of the cell was 0.79 cm². A membrane resistance, (R, in Ω cm²) was calculated as follows:

$$\mathbf{R} = (\mathbf{R}_1 - \mathbf{R}_2) \times \mathbf{S} \tag{1}$$

An ionic conductivity was calculated by Eq. (2).

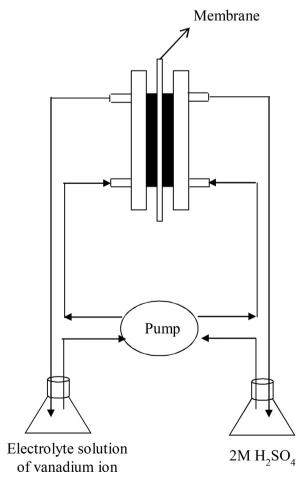
$$IC = 1/R \times L$$
⁽²⁾

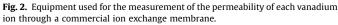
where, IC $(S\,cm^{-1})$ is an ionic conductivity, R $(\Omega\,cm^2)$ is a membrane resistance, L (mm) is a membrane thickness.

Permeability of the vanadium ions

The measurement method and experimental apparatus for the permeability of the vanadium ions are the same with the previous paper [7].

Fig. 2 shows the equipment to measure the permeability of each vanadium ion through a commercial ion exchange membrane. One reservoir was filled with $2 \text{ M H}_2\text{SO}_4$ aq. solution of 50 cm^3 and the other reservoir was filled with an electrolyte solution of vanadium ion of 50 cm^3 . Both solutions were circulated through the cell compartments of the redox flow cell which were separated by an





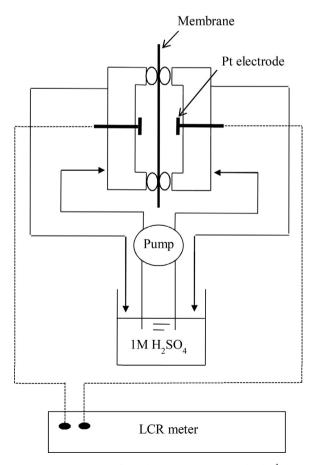


Fig. 1. Measuring equipment of membrane resistance in $1\,M~(mol\,L^{-1})~H_2SO_4$ aq. solution.

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